

260900



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IMPROVEMENTS IN AND RELATING TO ACID-TYPE DETERGENTS

We Hi-Tech Detergents Limited, a New Zealand company of
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hereby declare the invention for which We pray that a patent may be
granted to us, and the method by which it is to be performed to be
particularly described in and by the following statement:

IMPROVEMENTS IN AND RELATING TO ACID-TYPE DETERGENTS

TECHNICAL FIELD

The present invention is directed towards detergents. More specifically, most aspects of the present invention are directed towards acid-type
5 detergents which find a variety of uses, including the cleaning of dairy plant. Their use in conjunction with the cleaning of dairy related plant will also be discussed.

BACKGROUND ART

Acid detergents are used for a variety of applications. In particular, they
10 find widespread use in the cleaning of dairy and milking plant as they are effective in cleaning many of the deposits left by milk on equipment. Alkaline detergents are also used in cleaning dairy plant, though the acid detergents are generally effective in removing deposits left after alkaline washing. Most dairy plant is of stainless steel and thus the
15 acidic nature of the detergent does not generally represent a problem. However, some acids, and acid combinations (e.g hydrochloric acid in combination with an oxidising acid or agent) would however be inadvisable as being corrosive to the plant.

Traditionally acid detergents for dairy related use comprise mixtures of
20 sulfuric and phosphoric acids. However, while sulfuric acid is a strong acid, phosphoric acid undergoes several successive dissociation (of H^+) steps. Each progressive dissociation step has its own equilibrium which, unfortunately, results in a relatively effective buffer in certain circumstances. One such instance is in the presence of other strong
25 acids (see later) where very little of the phosphoric acid is actually dissociated. Accordingly, it could be argued that the contribution of

phosphoric acid in acid detergents is relatively limited as the phosphoric acid component will only be truly effective once the dissociated hydrogen ion from the other acids has been consumed. Often by this stage the solution is buffered at a substantially neutral or alkaline pH or the solution is in the alkaline region.

A further disadvantage of the phosphoric based acid detergent is that while the unused phosphoric acid and any phosphate products are biodegradable, these compounds are strongly associated with the unwanted eutrophication of waterways. Accordingly, there is some consumer pressure, prompted by the current green movement, to find acceptable alternatives. There is also the ever present possibility that legislation may be enacted to address the entry of phosphate compounds into waterways.

A further problem associated with phosphoric acid based acid detergents is that they appear to be adversely affected by the presence of iron and manganese ions in the water. Unfortunately, most New Zealand water supplies, especially on farms where supplies often come from bores or streams, often have high or significant proportions of these ions. Accordingly, unless this is taken into account when mixing the detergent for use, a working wash fluid may not be as effective as believed. This may cause further problems as overdiluted detergent solutions (in which there is insufficient acid) may need to rely on the further dissociation of hydrogen ions from partially dissociated anionic phosphate species. As previously mentioned these protons are often only released in substantially neutral or alkaline conditions - an overdiluted (or ion impaired) detergent solution may end up being an alkaline wash, and/or not effective at all.

Furthermore, apart from the strongly acidic nature of the solution, neither phosphoric nor sulfuric acid specifically confer any antibacterial properties to the diluted detergent. In some instances residual phosphate could even provide a useful nutrient to accelerate the growth of certain micro-organisms. Accordingly, antibacterial properties must be conferred by the addition of additional antibacterial agents when this property is desired.

It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

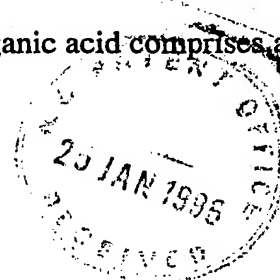
10 DISCLOSURE OF INVENTION

According to one aspect of the present invention there is provided an acid detergent comprising an acid detergent composition comprising:

- at least one inorganic acid (as herein defined) other than phosphoric acid, in combination with
- 15 - at least one organic acid (as herein defined), and
- at least one of a surfactant, sanitiser, and a quaternary ammonium salt; the detergent being further characterised in that, when reacted with an alkaline material, greater than 75% of available protons are made available at a pH of 4.5 or less.

- 20 According to another aspect of the present invention there is provided an acid detergent composition substantially as described above in which a said inorganic acid comprises a member of the group: sulfuric acid, sulfamic acid, an oxysulfur acid, hydrochloric acid, and nitric acid.

- 25 According to another aspect of the present invention there is provided an acid detergent composition substantially as described above in which a said organic acid comprises a monocarboxylic acid.



According to another aspect of the present invention there is provided an acid detergent composition substantially as described above in which a said organic acid comprises at least one of: a dicarboxylic acid, a polycarboxylic acid, an acidic phenol.

According to another aspect of the present invention there is provided an acid detergent composition substantially as described above in which, when reacted with alkaline material, greater than 75% of available protons are made available at a pH of 4.5 or less.

According to another aspect of the present invention there is provided an acid detergent composition substantially as described above in which, when reacted with alkaline material, at least 85% of available protons are made available at a pH of 5 or less.

According to another aspect of the present invention there is provided an acid detergent composition substantially as described above in which the components are miscible with each other.

According to another aspect of the present invention there is provided an acid detergent composition comprising, by weight, to a total of 100%:

0.001-95% at least one organic acid

0.001-50% at least one mineral acid other than phosphoric acid

0-75% water or diluent

$0 < x < 20\%$ other optional components including at least one of a surfactant, sanitiser, and quaternary ammonium salt

the resulting composition being further characterised such that, when reacted with an alkaline material, greater than 75% of available protons are made available at a pH of 4.5 or less.

According to another aspect of the present invention there is provided a method of cleaning equipment contaminated with milk and dairy products comprising flushing, or bringing into contact, said equipment



with an acid detergent composition comprising an inorganic acid other than phosphoric acid in combination with an organic acid (as herein defined) and optionally a sanitiser.

5 According to another aspect of the present invention there is provided a method for the manufacture of an acid detergent composition as claimed in any one of claims 1 through 21, comprising the preparation of said inorganic acid to the required dilution, and subsequently combining said organic acid.

10 According to another aspect of the present invention there is provided a working strength acid detergent composition as claimed in any one of claims 1 through 21 which includes, by weight, 0.001 - 1.0% of inorganic acid, and 0.001 - 1.5% of organic acid.

15 The present invention provides an acid detergent which in its simplest form comprises a mineral acid in combination with an organic acid. The term 'mineral acid' will be used in its normal sense and shall be taken to comprise acids other than organic acids. Preferably, but not necessarily, the mineral acid will comprise a monoprotic or diprotic acid. Lewis acids may also find use as mineral acids.

20 The term 'organic acid' will be used in the normal sense also and generally comprises acids based on, or containing, carbon. Typically organic acids will include carboxylic acids though phenols (preferably acidic phenols) may also find use within the present invention. Sulfamic acid shall be classed herein as a mineral acid, though as it is sometimes classified as an organic acid, it could conceivably find use as an organic acid within the present invention.

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While a wide range of mineral acids may be used in various embodiments of the present invention, consideration will need to be given to factors such as costs, compatibility with other components of the detergent and the effect on the equipment to be cleaned. For instance, hydrochloric acid is not generally advisable for use in many stainless steels as in the presence of many oxidising agents it can readily attack the metal. However, where the surface to be cleaned is predominantly glass or plastic, then there may be no problem with using hydrochloric acid. The same considerations will also apply to other acids. In a preferred embodiment of the present invention for use on dairy plant, which typically comprises stainless steel, an oxysulfur acid such as sulfuric acid will typically be employed. The other oxysulfur acids, and also including sulfamic acid, may also be used or present.

To avoid the problems associated with phosphoric acid (see later) it is preferable that strong acids which readily dissociate are relied upon. Sulfuric acid is one such acid. Hydrochloric and nitric acid are also considered strong acids with a high degree of dissociation. However they may be unsuitable because of their corrosive action on certain substances, either on their own or in combination with other substances.

Often the mineral acid will be a monoprotic or diprotic acid though polyprotic acids could also be used. The key however is to avoid a situation such as with a polyprotic acid such as phosphoric acid where the degree of dissociation in the presence of other strong acids is not strong and under certain conditions a buffering arrangement may be set up. Ideally most acidic protons will be available at a pH of 5 or less.

- Calculations have been given to determine the degree of dissociation in phosphoric in combination with nitric and sulfuric acids. As can be appreciated from the calculations below, the degree of dissociation of phosphoric acid may be as little as 2%. Clearly the phosphoric acid is making relatively little contribution as an acid in the overall system.

DISSOCIATION WITH PHOSPHORIC ACID IN A MIXTURE WITH STRONG NITRIC ACID

In a $\text{HNO}_3/\text{H}_3\text{PO}_4$ mixture there appears to be
 $[\text{H}^+] \quad \quad \quad = 0.267 \text{ mol/l}$
 $[\text{H}_2\text{PO}_4^-] \quad \quad \quad = 0.001 \text{ mol/l}$
 $[\text{NO}_3^-] \quad \quad \quad = 0.266 \text{ mol/l}$ } in diluted solution

i.e. only 2% of the H_3PO_4 has dissociated.

$[\text{HPO}_4^{2-}]$ at about 10^{-10} is near enough to zero.

840 parts 70% HNO_3 } parts by volume
 150 parts 85% H_3PO_4 }

$$\text{mass HNO}_3 = 840 \text{ ml} \times 1.42 \text{ g/ml} \times 0.70 = 835 \text{ g}$$

$$\text{mass H}_3\text{PO}_4 = 150 \text{ ml} \times 1.69 \text{ g/ml} \times 0.85 = 215 \text{ g}$$

$$\text{amount HNO}_3 = \frac{835 \text{ g}}{63.0 \text{ g mol}^{-1}} = 13.3 \text{ mol}$$

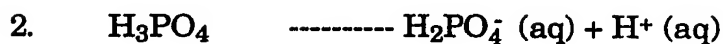
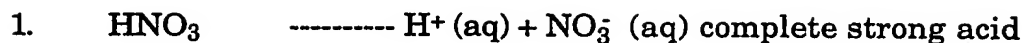
$$\text{amount H}_3\text{PO}_4 = \frac{215 \text{ g}}{98.0 \text{ g mol}^{-1}} = 2.19 \text{ mol}$$

Assume no volume change on mixing of concentrated acids and dilute to 2% v/v

$$0.990 \text{ l} \quad \rightarrow \quad 49.5 \text{ l} \approx 50 \text{ l}$$

$$[\text{CHNO}_3] = \frac{13.3 \text{ mol}}{50 \text{ l}} = 0.266 \text{ mol/l}$$

$$[\text{H}_3\text{PO}_4] = \frac{2.19 \text{ mol}}{50 \text{ l}} = 0.044 \text{ mol/l}$$



$$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.4 \times 10^{-3} \text{ mol/l ignore } K_{a2} \text{ and } K_{a3}$$

let $[\text{H}^+]_2 = x$

$$\frac{(0.266 - x)(x)}{(0.044 - x)} = 7.4 \times 10^{-3}$$

$$x^2 + 0.266x = 3.26 \times 10^{-4} - 7.4 \times 10^{-3}x$$

$$x^2 + 0.273x = 3.26 \times 10^{-4} \quad x = 3.26 \times 10^{-4} \quad x = 0$$

and x

$$-0.273 \pm \sqrt{0.273^2 - 4 \times 3.26 \times 10^{-4}} = 1.2 \times 10^{-3} \text{ \& checks}$$

$$[\text{H}^+] = 0.267 \text{ mol/l}$$

$$[\text{H}_2\text{PO}_4^-] = 0.001 \text{ mol/l i.e. } \approx 2\% \text{ H}_3\text{PO}_4 \text{ dissociates}$$

$$[\text{NO}_3^-] = 0.266 \text{ mol/l}$$

$$\text{look at } K_{a2} = 6.3 \times 10^{-8} \text{ mol/l} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$\frac{6.3 \times 10^{-8}}{2.7 \times 10^{-1}} \approx 2 \times 10^{-7} = \frac{[\text{HPO}_4^{2-}]}{1 \times 10^{-3}}$$

$$[\text{HPO}_4^{2-}] \approx 10^{-10} \text{ i.e. none}$$

and

$$[\text{PO}_4^{3-}] \text{ much less}$$

DISSOCIATION OF PHOSPHORIC ACID IN A MIXTURE WITH
STRONG SULFURIC ACID

$[H^+]$	$= 1.7 \cdot 10^{-2} \text{ mol/l}$		
$[HSO_4^-]$	$= 5.4 \cdot 10^{-3} \text{ mol/l}$	}	
$[H_2PO_4^-]$	$= 4.6 \cdot 10^{-3} \text{ mol/l}$	}	in diluted solution
$[SO_4^{2-}]$	$= 3.3 \cdot 10^{-3} \text{ mol/l}$	}	
$[H_3PO_4]$	$= 1.0 \cdot 10^{-2} \text{ mol/l}$	}	

i.e there is twice as much H_3PO_4 as there is $H_2PO_4^-$.

300 g 85% H_3PO_4

150 g 98% H_2SO_4

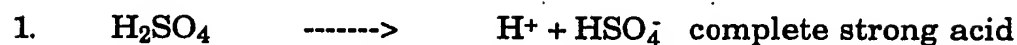
mass H_3PO_4	$= 300 \text{ g} \times 0.85$	$= 255 \text{ g}$
amount H_3PO_4	$= \frac{255 \text{ g}}{98.0 \text{ g} \cdot \text{l}^{-1}}$	$= 2.60 \text{ mol}$
mass H_2SO_4	$= 150 \text{ g} \cdot 0.98$	$= 147 \text{ g}$
amount H_2SO_4	$= \frac{147 \text{ g}}{98.1 \text{ g} \cdot \text{l}^{-1}}$	$= 1.50 \text{ mol}$
$v_{H_3PO_4}$	$= \frac{300 \text{ g}}{1.69 \text{ g} \cdot \text{ml}^{-1}}$	$= 175 \text{ ml}$
$v_{H_2SO_4}$	$= \frac{150 \text{ g}}{1.84 \text{ g} \cdot \text{ml}^{-1}}$	$= 82 \text{ ml}$

Assume no volume change on mixing i.e., $V_{\text{total}} = 258 \text{ ml}$ and dilute to 0.15% by volume

$$v_{\text{mixture}} = \frac{0.258 \text{ l}}{0.0015} = 172 \text{ l}$$

$$c_{\text{H}_3\text{PO}_4} = \frac{2.60 \text{ mol}}{172 \text{ l}} = 1.5 \times 10^{-2} \text{ mol/l}$$

$$c_{\text{H}_2\text{SO}_4} = \frac{1.50 \text{ mol}}{172 \text{ l}} = 8.7 \times 10^{-3} \text{ mol/l}$$



$$K_{a2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 1.0 \times 10^{-2} \text{ mol/l}$$



$$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.4 \times 10^{-3} \text{ mol/l}$$

Ignore K_{a2} and K_{a3}

Let $[\text{H}^+]_2 = x$ and $[\text{H}^+]_3 = y$

$$\frac{(8.7 \times 10^{-3} + x + y)(x)}{(8.7 \times 10^{-3} - x)} = 1.0 \times 10^{-2}$$

and

$$\frac{(8.7 \times 10^{-3} + x + y)(y)}{(1.5 \times 10^{-2} - y)} = 7.4 \times 10^{-3}$$

and solve for x and y

$$x = 3.3 \times 10^{-3} \text{ mol/l and } y = 4.6 \times 10^{-3} \text{ mol/l}$$

$$[\text{H}^+] = 1.7 \times 10^{-2} \text{ mol/l}$$

$$[\text{HSO}_4^-] = 5.5 \times 10^{-3} \text{ mol/l}$$

$$[\text{H}_2\text{PO}_4^-] = 4.6 \times 10^{-3} \text{ mol/l}$$

$$[\text{SO}_4^{2-}] = 3.3 \times 10^{-3} \text{ mol/l}$$

$$[\text{H}_3\text{PO}_4] = 1.0 \times 10^{-2} \text{ mol/l}$$

As can be appreciated from the foregoing calculations, the use of phosphoric acid in acid detergent formulations with other strong mineral acids is not entirely effective.

- 5 In order to replace phosphoric acid as a main acid the present invention proposes the use of an organic acid in conjunction with one or more inorganic acids. The preferred organic acids are C₁₋₁₀ carboxylic acids and this may include both alkyl and aromatic acids. More preferably the acid will be a monocarboxylic acid and miscibility with water or the chosen diluent is also a preferred characteristic.
- 10 Several preferred organic acids include formic acid, glycolic acid, and acetic acid. Formic acid in conjunction with mineral acid is used in a preferred embodiment of the present invention and can provide some improvements over phosphoric acid. For instance, formic acid does not contribute to eutrophication of waterways as does phosphoric acid, yet is
- 15 still biodegradable. It also exhibits antibacterial properties and thus increases the antibacterial properties of an acid detergent which may not require the use of added antibacterial components.

- Furthermore, formic acid is not influenced by the presence of iron or manganese ions in the water supply, and is effective, as are many
- 20 simpler organic acids, in removing rust.

- A further difference is that many organic acids are not as aggressive towards stainless steel and other metals as are some other mineral acids such as hydrochloric and nitric acids. This would also appear to get around the potentially corrosive nature of a sulfuric/hydrochloric acid
- 25 mix and the highly oxidising/nitrating properties of a hydrochloric/nitric or sulfuric/nitric acid combination which can, in the right conditions,

oxidise or convert many organic compounds into explosive or flammable nitrates. The combination of organic acid with mineral acid appears to be acceptable with respect to corrosion of equipment. Consideration would need to be given to the use of concentrated oxidising acids in combination with organic acids. Preferably the dilution of the oxidising agent is sufficiently low as not to react, at least in the short term, with other included components.

- Formic acid in combination with sulfuric acid also appears to make the bulk of hydrogen ions available at low pH. Titrations have shown that for sulfuric and formic acid compositions there is a first gradual end point at a pH of around 2 and a major end point which begins at a pH of approximately 4.6 and extends beyond a pH of 9. The plot of pH against the titrant indicates that a major proportion (approximately 85%) of the available protons in this composition are consumed at a pH of less than 5.
- In contrast, the titration plot for compositions including phosphoric acid shows several additional end points at pHs of approximately 4.5 or greater and these end points consume approximately 25% of the titre i.e. a significant portion of the available acid protons are only available in substantially neutral through alkaline conditions.
- Unfortunately, for an effective acid detergent, it is desirable that the available acid protons are available at a pH of less than 5. If not then generally more acid must be provided to ensure that the pH remains below 5 if the detergent is to be truly effective. For instance, if alkaline materials are present in a milkline and the quantity present is the equivalent of approximately 80-90% of the titre in the titration experiments, then the pH of a sulfuric/formic acid mixture would remain below 4.5. However, for a phosphoric acid containing composition

the pH would be approximately 6-8 depending upon the exact formulation. Accordingly, the phosphoric acid system fails when it is being worked near its limit, which is the case when there are excessive deposits or incorrect dosing occurs some farmers attempt to 'economize' by using less detergent than they should.

Embodiments of the present invention may include additional mineral acids. While single inorganic acids have been identified, mixtures of two or more inorganic acids may also be considered. One preferred additional inorganic acid is sulfamic acid, which can be used in combination with sulfuric acid. Alternatively, sulfamic acid may sometimes be used as a substitute for sulfuric acid. It is also possible that phosphoric acid may also be included as an additional mineral acid, or less preferably even as the main mineral acid, with no other mineral acids present. However, it is envisaged that such phosphoric acid containing compositions will only be used in a few specialised compositions where other attributes of phosphoric acid may be desirable.

Similarly, additional organic acids may also be included in various compositions according to the present invention. Such additional organic acids will typically also be carboxylic acids or phenols and fall within the preferred set of C_{1-10} monocarboxylic acids. Dicarboxylic acids such as citric acid as well as other polycarboxylic acids may be employed in various embodiments of the present invention. While the preference for the main organic acid is a monocarboxylic acid, dicarboxylic and polycarboxylic acids may also be employed. For most embodiments of the present invention formic acid is preferred over the other organic acids,

and acetic or citric acids are preferred as additional organic acids. However this is not to preclude the use of other combinations of organic acids.

5 Other components may also be added into various embodiments of the present invention. For instance, sanitising agents are often included in acid detergents that will typically find use in embodiments of the present invention. Often these comprise quaternary ammonium salts. Other substances may also be used in various embodiments.

10 Surfactants will also optionally be included according to the requirements and end uses of various compositions.

BRIEF DESCRIPTION OF DRAWINGS

15 Further aspects of the present invention will become apparent from the ensuing description which is given by way of example only and with reference to the accompanying drawings which were those accompanying the provisional specification in which:

Figure 1 is a titration plot of a composition comprising formic, phosphoric and sulfuric acids in the proportion 11.7:30.0:12.0,

Figure 2 is a titration plot of formic, phosphoric and sulfuric acids in the ratios 20:10:12, and

20 Figure 3 is a titration plot of a composition comprising formic and sulfuric acids in the proportion of 2.5:9.8.

BEST MODES FOR CARRYING OUT THE INVENTION**Example 1**

According to one composition according to the present invention there is provided a composition for an acid detergent comprising, by weight to a total of 100%:

- 0.001-95% an organic acid comprising a C₁₋₁₀ monocarboxylic acid:
- 0.001-50% mineral acid other than phosphoric acid
- 0-75% water or diluent
- 0-20% other optional components;

Example 2

According to a second composition for an acid detergent according to the present invention, by weight to a total of 100%:

- 15-40% organic acid (water soluble);
- 5-20% mineral acid other than phosphoric acid
- 0-10% optional components
- remainder - water or diluent

Example 3

Essentially the compositions of examples 1 and 2 except that the organic acid component may comprise one or more organic acids. Similarly the mineral acid components may comprise one or more mineral acids.

Example 4

A composition according to any one of examples 1 through 3 in which the preferred mineral acid is sulfuric acid or an oxysulfur acid including sulfamic acid.

Example 5

A composition according to any of Examples 1 through 4 in which the organic acid comprises a C₁₋₁₀ monocarboxylic acid, which is water soluble.

5 Example 6

A composition according to any one of the preceding examples wherein the organic acid comprises at least one member of a group comprising formic acid, acetic acid, glycolic acid and citric acid.

Example 7

- 10 An acid detergent prepared according to the following method:

100 mls of 98% sulfuric acid is dissolved in approximately 500 mls of water. To this is added approximately 300 mls of 85% formic acid. Any additional sanitising agents and/or surfactants are also included into this composition which may then be diluted further to prepare working
15 solutions.

- Care should be taken that concentrated solutions of formic acid do not come into contact with concentrated sulfuric acid. The result can be the liberation of carbon monoxide and it is desirable that where combinations of sulfuric and formic acids are used, there is sufficient water to
20 minimise the essentially dehydrating decomposition of formic acid, by the concentrated sulfuric acid, into water and carbon monoxide.

Accordingly some preliminary trials may be performed when putting various embodiments of the present invention into practice to ensure that carbon monoxide is not liberated at a rate in the acid detergent

concentrate which will cause problems with the intended storage and shelf life of the product. It is noted that concentrated formic acid will slowly decompose to give various decomposition products with time and thus some minor liberation of carbon monoxide of other products may occur anyway. Accordingly care should be taken that the proportions and concentrations of components present are not sufficient to give the resulting product an excessively short and impractical shelf life.

Care should also be taken when combining certain organic acids with strongly oxidising acids such as nitric and various oxyhalo acids. The results may be unstable or explosive.

Example 8

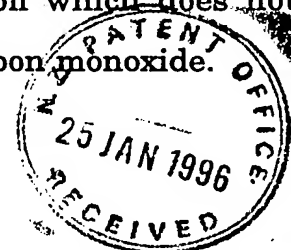
According to this example there is provided a working strength composition comprising an effective amount of an acid detergent according to the preceding examples in water or a diluent. In most instances the working strength solution will comprise approximately 0.01-2.5% acid detergent in water. To some extent this will depend upon the proportions of components in the acid detergent.

For cleaning milking plant, the acid detergent of the immediately preceding example is optimally diluted to 0.1-0.25% in water.

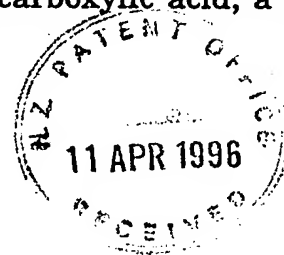
Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof as defined in the appended claims.

WHAT WE CLAIM IS:

1. An acid detergent composition comprising:
 - at least one inorganic acid (as herein defined) other than phosphoric acid, in combination with
 - at least one organic acid (as herein defined), and
 - at least one of a surfactant, sanitiser, and a quaternary ammonium salt; the detergent being further characterised in that, when reacted with an alkaline material, greater than 75% of available protons are made available at a pH of 4.5 or less.
2. An acid detergent composition as claimed in claim 1 in which a said inorganic acid comprises a member of the group: sulfuric acid, sulfamic acid, an oxysulfur acid, hydrochloric acid, and nitric acid.
3. An acid detergent composition as claimed in either claim 1 or claim 2 in which a said organic acid comprises a monocarboxylic acid.
4. An acid detergent composition as claimed in claim 3 in which a said organic acid comprises at least one of: formic acid, acetic acid, and glycolic acid.
5. An acid detergent composition as claimed in either claim 1 or claim 2 in which a said organic acid comprises at least one of: a dicarboxylic acid, a polycarboxylic acid, an acidic phenol.
6. An acid detergent composition as claimed in claim 5 in which a said organic acid comprises citric acid.
7. An acid detergent composition as claimed in either claim 1 or 2 which comprises sulfuric and formic acids in a combination which does not result in the ready decomposition of formic acid to carbon monoxide.



8. An acid detergent composition as claimed in any one of the preceding claims in which, when reacted with alkaline material, at least 85% of available protons are made available at a pH of 5 or less.
9. An acid detergent composition as claimed in either claim 7 or claim 8 which includes a phosphoric acid.
10. An acid detergent composition as claimed in any one of the preceding claims whose pH is 2.5 or less.
11. An acid detergent composition as claimed in any one of the preceding claims whose pH, when diluted to working strength for use in cleaning dairy equipment, is 4 or less.
12. An acid detergent composition as claimed in any one of the preceding claims in which the components are miscible with each other.
13. An acid detergent composition comprising, by weight, to a total of 100%:
- | | |
|----------------|-----------------------------------------------------------------------------------------------------------|
| 0.001-95% | at least one organic acid |
| 0.001-50% | at least one mineral acid other than phosphoric acid |
| 0-75% | water or diluent |
| $0 < x < 20\%$ | other optional components including at least one of a surfactant, sanitiser, and quaternary ammonium salt |
- the resulting composition being further characterised such that, when reacted with an alkaline material, greater than 75% of available protons are made available at a pH of 4.5 or less.
14. An acid detergent composition as claimed in claim 13 in which said organic acid comprises at least one of: a C₁₋₁₀ monocarboxylic acid, a di- or poly- carboxylic acid, and an acidic phenol.



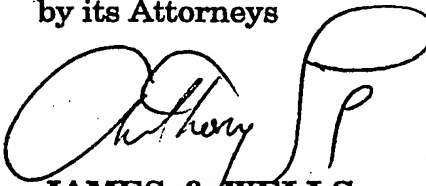
15. An acid detergent composition as claimed in either claim 13 or claim 14 in which said mineral acid comprises at least one of : sulfuric acid, sulfamic acid, an oxysulfur acid, hydrochloric acid, and nitric acid.
16. An acid detergent composition as claimed in any one of claims 13 through 15 in which an optional component includes at least one of: sulphamic acid, phosphoric acid, a surfactant, a sanitiser, and a quaternary ammonium salt.
17. An acid detergent composition as claimed in any one of claims 13 through 16 in which, when reacted with alkaline material, greater than 75% of available protons are made available at a pH of 4.5 or less.
18. An acid detergent composition as claimed in any one of claims 13 through 16 in which, when reacted with alkaline material, at least 85% of available protons are made available at a pH of 5 or less.
19. An acid detergent composition of the type claimed in the preceding claims, substantially as described herein with reference to the drawings and examples.
20. A method of cleaning equipment contaminated with milk and dairy products comprising flushing, or bringing into contact, said equipment with an acid detergent composition comprising an inorganic acid (as herein defined) other than phosphoric acid in combination with an organic acid (as herein defined) and optionally a sanitiser.
21. A method as claimed in claim 20 in which the acid detergent composition is a composition as claimed in any one of claims 1 through 19.
22. A method of the type claimed in claims 23 and 24, substantially as described herein with reference to the contained examples.



23. A method for the manufacture of an acid detergent composition as claimed in any one of claims 1 through 19, comprising the preparation of said inorganic acid to the required dilution, and subsequently combining said organic acid.
24. A method for the manufacture of an acid detergent composition, substantially as described herein, with reference to Example 7.
25. A working strength acid detergent composition as claimed in any one of claims 1 through 19 which includes, by weight, 0.001 - 1.0% of inorganic acid, and 0.001 - 1.5% of organic acid.

HI-TECH DETERGENTS LIMITED

by its Attorneys


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END